

# Conductivity Degradation Study of polypyrrole and polypyrrole/5% w/w TiO<sub>2</sub> nanocomposite under Heat Treatment in Helium and Atmospheric Air

E. Vitoratos, S. Sakkopoulos, E. Dalas, K. Emmanouil

**Abstract** — The thermal aging of the d.c. electrical conductivity  $\sigma$  in pure polypyrrole (PPy) and in the nanocomposite PPy/5%w/w TiO<sub>2</sub> was investigated for thermal treatment times from 0 to 50 hours at different temperatures T = 100, 300 and 380 K under atmospheric air and inert He gas. In both materials the fluctuation induced tunneling of charge carriers was followed revealing a granular metal structure. The isothermal variation of  $\sigma$  with time under atmospheric air and inert He indicates the coexistence of two antagonistic mechanisms, the one increasing and the other decreasing  $\sigma$ . In XRD patterns from PPy and PPy/5%w/w TiO<sub>2</sub> the sharp peaks of rutile and anatase crystallographic types of TiO<sub>2</sub> coexist with the broad peak of amorphous PPy. The latter shifts to smaller angles with the addition of TiO<sub>2</sub> indicating a greater separation of pyrrole rings, which turns up to be about equal to the diameter of O<sup>2-</sup> indicating the diffuse of oxygen from TiO<sub>2</sub> into PPy. SEM pictures confirm the removal of Cl<sup>-</sup> in the form of HCl during thermal aging, a process which decreases the conductive part of the polymer and at the same time rearranges the chains. These represent two antagonistic mechanisms the first decreasing, the second increasing conductivity.

**Index Terms**— Conducting polymers, Conductivity degradation mechanisms, Thermal stability, nanocomposites

## I. INTRODUCTION

Among conjugated polymers, polypyrrole exhibits high electrical conductivity, environmental stability and strong absorption along the visible spectrum to near infrared [1 – 3]. Hybrid polymer/inorganic semiconductor composites exhibit interesting electronic and optical properties which make them suitable as active elements in solar cells, photocatalysts and supercapacitors [4-6]. A very serious problem with conjugated polymers is their degradation under environmental conditions. This undesirable process is very complicated including dedoping, oxidation, hydrolysis and scission of the polymer chains induced by the atmospheric oxygen and moisture, as well as crosslinking of the chains, which destroys the conjugated character of them [7-9]. The study of the degradation mechanisms is very important as it is the only way to act properly on them to delay this deterioration [10]. The purpose of this work is to examine the thermal aging of HCl protonated pure PPy and PPy/5%w/w

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TiO<sub>2</sub> nanocomposite, as it appears with the decrease of their d.c. conductivity, in connection to their structure. Of special interest is the role of atmospheric oxygen and moisture, as well as the possibility of oxygen diffusion from TiO<sub>2</sub> into PPy for the aging, relevant to the lifetime of organic electronic devices working under environmental conditions.

## II. EXPERIMENTAL

Conductive PPy and PPy/5% w/w TiO<sub>2</sub> samples were prepared by polymerization of distilled pyrrole with FeCl<sub>3</sub> (monomer/oxidant = 1:1 mol/mol) in HCl acid – water solutions at pH = 2.00 mixed with the proper ratio with TiO<sub>2</sub> nanoparticles with nominal diameter of 25 nm (Degussa AG Germany) in an ice bath under a nitrogen atmosphere [11]. The pristine PPy and the PPy/5% w/w TiO<sub>2</sub> nanocomposite were obtained as black precipitates, which were purified by Soxhlet extraction for 35 h. After drying for 24 h, the precipitates were compressed in an IR press under a 10 tn/cm<sup>2</sup> pressure for about 15 min. By this way disc shaped specimens of about 13 mm in diameter and 1.5 mm thick were obtained. The d.c. conductivity measurements vs temperature were performed using a four – probe method [12] in a cryostat filled with inert He or atmospheric air. The temperature was monitored by an Oxford intelligent temperature controller (ITC4). A Kithley 2400 sourcemeter and a Keithley 182 sensitive digital voltmeter were used to control the current and voltage respectively and measured them automatically via a PC. XRD patterns were obtained on a Siemens D – 5000 diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and SEM images were taken by a Zeiss SUPRA 35VP Scanning Electron Microscope.

## III. RESULTS AND DISCUSSION

### D.C. Electrical conductivity

The thermal treatment of PPy and PPy/TiO<sub>2</sub> nanocomposite at 380 K for 0 to 36 h under room atmosphere had as a result the aging of the samples, as it is shown from the  $\sigma = f(T)$  curves in Fig.1.

The conductivity  $\sigma$  is thermally activated according to

$$\sigma = \sigma_0 \exp\left(-\frac{T_1}{T+T_0}\right) \quad (1)$$

indicating a granular metal model structure in which conduction takes place through a fluctuation induced tunneling [13,14].

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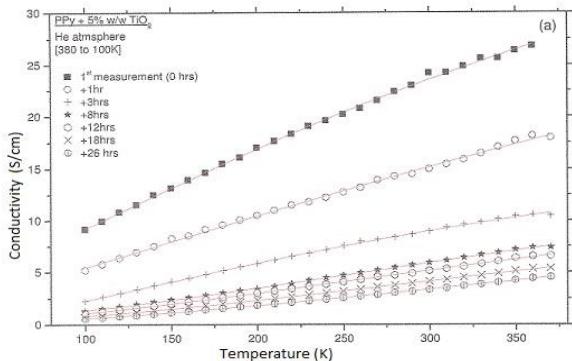


Fig.1. The decrease of the electrical conductivity (aging) of a PPy/5% w/w TiO<sub>2</sub> due to heating in room atmosphere at 380 K for different times from 0 to 26 h.

The rate  $d\sigma/dT$  of PPy samples is about twice as large as in PPy/TiO<sub>2</sub> indicating that the presence of TiO<sub>2</sub> makes more difficult the thermal activation of carriers, as its energy gap (3.2 eV) is larger than that of PPy (2.5 eV). In a material with the granular metal structure thermal degradation takes place in a corrosion – like process which reduces the size of the conductive grains and so enhances the potential barrier between them [1,2]. The parameter  $\sigma_0$  is a measure of the conductivity in the interior of the grains and remains practically constant during the thermal treatment, indicating that the conductivity in them is not affected by thermal aging. On the other hand, the parameters  $T_1$  and  $T_0$ , which depend on the height and the shape of the potential barriers between the grains [14], increase linearly with thermal treatment, indicating that conductivity becomes more difficult between the grains.  $T_1$  and  $T_0$  allow the calculation of  $s$ , the distance between the grains. This increases rapidly for the first 10 – 15 min of the heat treatment and then remains almost constant indicating that the conductive grains are surrounded by a shell, several angströms thick, which is not as stable as the core of them [15].

Thermal aging in a material with the granular metal structure, where the dimensions of the conductive grains diminish with the thermal treatment, reduces the conductivity according to the formula

$$\sigma = \sigma_0 \exp \left[ - \left( \frac{t}{\tau} \right)^{1/2} \right] \quad (2)$$

where  $\tau$  is the characteristic time of the degradation. The higher is  $\tau$  the slower is this undesirable process [1]. The presence of 5% TiO<sub>2</sub> slows down the aging process characteristic  $\tau$  by about 20%. This may be attributed to the reduction of the chain mobility by the presence of TiO<sub>2</sub> nanoparticles.

In Fig.2 the change of the reduced (relative to the initial value) conductivity of pure PPy and PPy/5% TiO<sub>2</sub> nanocomposite at 300 K for times from 0 to 200 min is shown, under room atmosphere and under inert He.

The shape of the isotherms shown in Fig.2 reveals the existence of two antagonistic mechanisms during the heat treatment at 300 K under room atmosphere, one increasing and the other decreasing the conductivity.

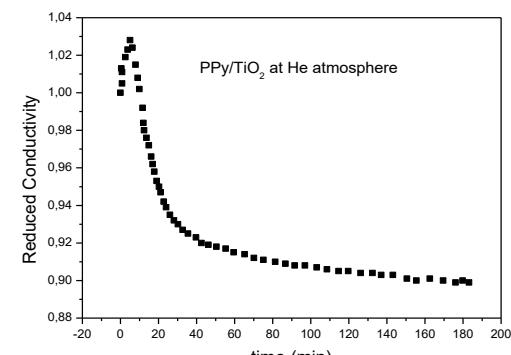
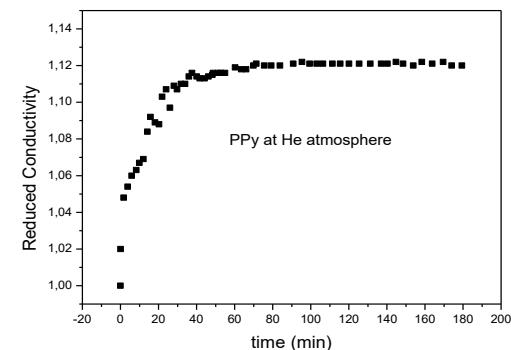
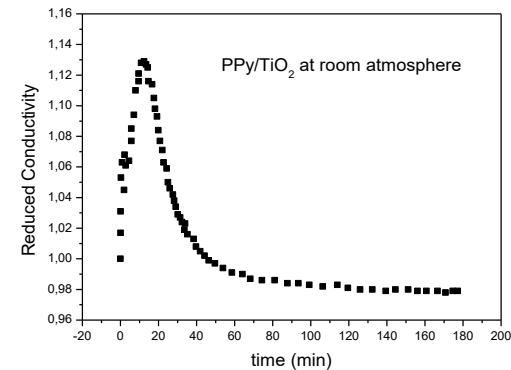
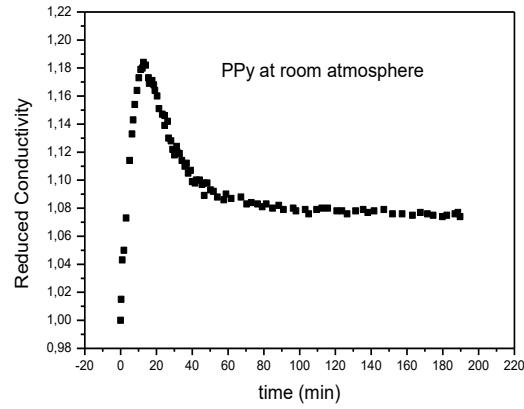


Fig.2. The reduced conductivity of pure PPy and PPy/TiO<sub>2</sub> at 300 K under inert He for times from 0 to 200 min.

For the first ~ 10 min the increase of the conductivity prevails and then the decrease predominates. A possible explanation is that the rearrangement of the polymer chains in the first stage of deprotonation, as it is shown in SEM pictures

(Fig.4), increases the conductivity, though after a while the other process prevails, by which oxygen, moisture and more intense deprotonation deteriorate the polymer chains reducing the conductivity.

From Fig.2 a completely different behaviour of PPy on the one hand and the PPy/5%TiO<sub>2</sub> under He atmosphere on the other is shown. The rearrangement of the polymer chains with deprotonation improves the conductivity of the pure PPy for the first 40 min and then equalization with the decrease of the conductivity from deprotonation is obtained. On the other hand, in PPy/5% TiO<sub>2</sub> the abrupt decrease of the conductivity after the first 10 min of heating is an indication that a transfer of oxygen from the TiO<sub>2</sub> surface to the polymer is taking place at 300 K, as elsewhere has been proved by UV – VIS spectroscopy [16].

The behaviour of pure PPy and PPy/5%w/wTiO<sub>2</sub> at 100 K vs time under room atmosphere resemble the curves of Fig.2, where two antagonistic processes are present, the one prevailing to the other at different time intervals. Under inert He atmosphere both materials behave as PPy in Fig.2, where an equilibrium of the two processes is obtained after a while. Finally, at 380 K for both materials and for both environments the behaviour resembles the curves of Fig.2.

#### X – ray Diffraction (XRD) patterns

Fig.3 presents XRD patterns of pure PPy, nanocomposite PPy/5%w/wTiO<sub>2</sub> and crystalline TiO<sub>2</sub>. PPy gives the characteristic broad peak at a diffraction angle  $2\theta = (22.5 \pm 0.5)^\circ$  indicating an amorphous character. From the Bragg's law

$$2d\sin\theta = \lambda \quad (3)$$

where  $\lambda = 1.5418 \text{ \AA}$ , the X – ray wavelength of Cu K $\alpha$  line, the closest distance d of approach of the planar aromatic rings of pyrrole is calculated

$$d = (4.0 \pm 0.1) \text{ \AA} \quad (4)$$

in accordance with the distance 4.5  $\text{\AA}$  between aromatic rings in PPy referred in literature [17].

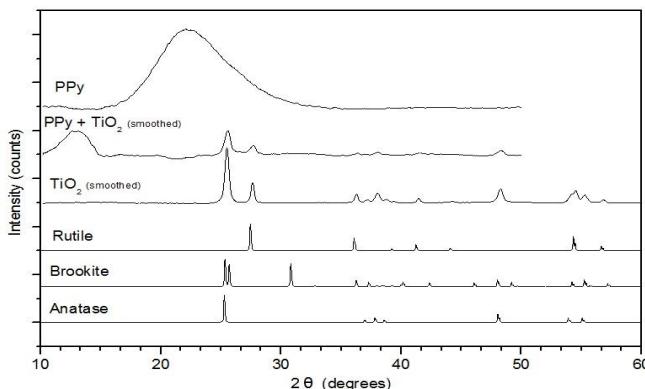


Fig.3. XRD spectrograms from pure PPy, PPy/5%w/wTiO<sub>2</sub> and TiO<sub>2</sub>. The XRD patterns of the crystallographic types rutile, brookite and atanase of TiO<sub>2</sub> are shown as well.

Crystalline TiO<sub>2</sub> gives sharp peaks which by comparison with data from PDF-3 base (International Centre for Diffraction Data) [18,19], indicate that the TiO<sub>2</sub> used is a mixture of rutile and anatase, but not brookite. From Debye - Scherrer equation

$$D = k\lambda/(\beta \cos\theta) \quad (5)$$

the average size D of the crystallites can be calculated, taking into account that the shape factor k = 0.89,  $\lambda = 1.5418 \text{ \AA}$ ,  $\beta$  the line - width measured at half – height of the peak and  $\theta$  the Bragg angle of diffraction in degrees. An approximate crystallite size of about 20 nm can be deduced from the intense peaks at  $2\theta = 26.0^\circ$  and  $27.8^\circ$  in accordance with the nominal nanoparticles size given from the supplier of TiO<sub>2</sub>, indicating that each nanoparticle consists of one crystallite.

The nanocomposite PPy/5% w/w TiO<sub>2</sub> gives a XRD spectrum in which the lines of TiO<sub>2</sub> superimpose the broad pattern of PPy. The lines are at the same angles but they become slightly broader, giving a crystallite size between 11 and 15 nm instead of 20 nm for pure TiO<sub>2</sub>. This decrease is an indication that oxygen from TiO<sub>2</sub> is transferred to PPy.

Moreover, the broad pattern of amorphous PPy in the nanocomposite shifts to smaller angles, its maximum being now at about  $2\theta = (13.2 \pm 0.5)^\circ$  instead of  $(22.5 \pm 0.5)^\circ$  in pure PPy. This decrease corresponds to a greater separation of  $d = (6.7 \pm 0.1) \text{ \AA}$  between pyrrole rings, instead of  $(4.0 \pm 0.1) \text{ \AA}$  in pure PPy. This significant increase is an additional indication that oxygen from TiO<sub>2</sub> is inserted between the PPy chains. This view is further supported from the fact that the radius of O<sup>2-</sup> is estimated to about 1.32 – 1.40  $\text{\AA}$  [20,21], i.e. a diameter of about 2.64 – 2.80  $\text{\AA}$ , almost equal to the difference of separation  $(6.7 - 4.0) = 2.7 \text{ \AA}$  between pyrrole rings in PPy and PPy/5% w/w TiO<sub>2</sub>.

#### Scanning Electron Microscopy (SEM)

From SEM pictures of pristine and thermally aged PPy it is confirmed the removal of Cl<sup>-</sup> in the form of HCl, as it is shown in Fig.4, by the decrease of the more light regions, which have higher atomic numbers containing more Cl<sup>-</sup> [22]. The removal of HCl deprotonates the polymer decreasing the amount of its conductive phase and so reduces its electrical conductivity. From the SEM pictures turns up that the thermal aging is accompanied by a smoothing of the sample surface, which is attributed to an improvement of the rearrangement of the polymer chains [23,24].

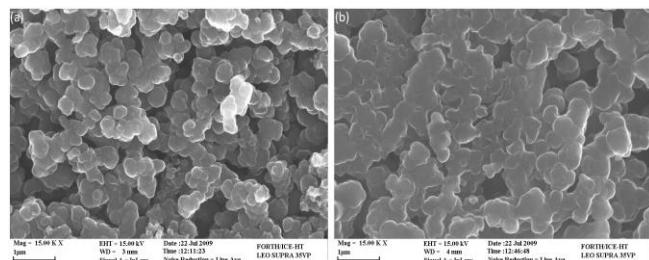


Fig.4. SEM pictures from pristine PPy on the left and thermally aged polymer at 380 K for 36 h on the right. The decrease of the more light regions and the smoothing of the surface with aging confirm the removal of Cl<sup>-</sup> and the rearrangement of the polymer chains.

The deprotonation and the rearrangement of the polymer chains have antagonistic results on the electrical conductivity, the first decreasing it by reducing the proportion of the conductive phase of the polymer, the other increasing the conductivity by facilitating the carriers hopping from the one chain to the other. From SEM pictures of higher resolution it has been apparent that the PPy grains have a size 15 – 30 nm,

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though the dimensions of the TiO<sub>2</sub> grains vary in the range 20 – 25 nm. It is accepted that the size of the conductive grains in PPy is about 20 nm [1], almost equal to those of TiO<sub>2</sub>. So, it seems that TiO<sub>2</sub> are arranged between the conductive grains increasing the potential barrier for carriers moving from the one of them to the other.

## IV. CONCLUSION

The thermal aging of pure conductive PPy and the nanocomposite PPy/5% w/wTiO<sub>2</sub> suitable for the construction of solar cells, has been investigated under atmospheric air and inert He. Although conductive polymers and their composites are easy and cheap to make, they are vulnerable of degradation under the oxygen and moisture of atmospheric air, which destroys the conjugated character of their chains. The study of the degradation mechanisms is very important as from this knowledge it is possible to find ways to decelerate this undesirable process. Both materials have the granular metal structure, where conductive grains shrinking with thermal aging by a corrosion– like process are embedded in an insulating background. The isothermal variation of the electrical conductivity  $\sigma$  of both materials with time reveals the existence of two antagonistic mechanisms, the one increasing and the other decreasing  $\sigma$ . From XRD patterns it is revealed that, apart from atmospheric air, oxygen is transferred from TiO<sub>2</sub> into PPy which contributes to the destruction of polymer chains reducing the conductivity. SEM pictures confirm the removal of Cl<sup>-</sup> in the form of HCl, a process which decreases the conductive phase of the polymer and at the same time rearranges its chains. So, two competing mechanisms for the change of the conductivity during thermal aging are revealed. The destruction of the conjugated character of PPy by oxygen from atmospheric air and TiO<sub>2</sub> and the decrease of the conductive part of the polymer diminish the conductivity, though the rearrangement of the polymer chains increases it. The study of the thermal aging of PPy/TiO<sub>2</sub> nanocomposites with different concentrations of TiO<sub>2</sub> will show the most stable composite suitable for photonic applications.

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